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# Monitoring of reduction reaction of 2-((phenylimino)methyl)phenol compound with sodium borohydride in solution by infrared spectroscopy

Onur Turhan and Hatice Yaşar

Department of Chemistry, Faculty of Arts and Sciences, Balıkesir University, Çağış, Turkey

#### ABSTRACT

In this study, an imine compound 2-((phenylimino)methyl)phenol was synthesized by the reaction of salicylaldehyde and aniline for in situ monitoring of reduction with sodium borohydride. The reduction of C = N double bond to C-N in solution was continuously monitored by infrared spectroscopy using the background defining method in liquid cell at ambient temperature. The structures of the purified 2-((phenylimino)methyl)phenol compound and the resulting 2-((phenylamino)methyl)phenol compound were elucidated by Infrared Spectroscopy,  $H^1$  and  $C^{13}$  Nuclear Magnetic Resonance Spectroscopy.

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KEYWORDS Background defining; imines; infrared spectroscopy; reaction monitoring; reduction

#### Introduction

Amines are important compounds used in organic chemistry as reagents or intermediates and in many industrial fields.<sup>[1]</sup> Amines are widely used as raw materials in polymer chemistry, solvents in organic chemistry, additives in the plastic and textile industries. It is also frequently used in the paint,<sup>[2]</sup> pharmaceutical<sup>[3]</sup> and food industry.<sup>[4]</sup> The amine derivatives obtained by the reaction of aldehydes and ketones with ammonia, primary or secondary amines in a reducing reagent medium are synthesized for use in biological and chemical processes.<sup>[5]</sup> Different substituted amine derivatives can be obtained by reducing the imines.<sup>[6]</sup>

Since amines are biologically important<sup>[7]</sup> and interesting compounds in addition to their use in many fields, the reaction of reducing imines to the amine examined in the study is also very important. Therefore, the reduction reaction of 2-((phenylamino) methyl) phenol, an imine compound, with NaBH<sub>4</sub> in methanol solvent was monitored by FT-IR.

The secondary amine compound (2-((phenylamino)methyl)phenol) in this study was obtained by reduction of the imine compound (2-((phenylimino)methyl)phenol) which obtained from the reaction of aniline with salicylaldehyde. The reaction medium of the imine to the amine was monitored in the FT-IR liquid cell by the background (bg) defining method.

There are methods in the literature for monitoring various organic reaction environments.<sup>[8-10]</sup> In the method used in the study, unlike other FT-IR methods, the beginning of the reaction was defined as the background (bg) and then the reaction environment was monitored by FT-IR. This method, which was previously used by us to monitor some imination reactions,<sup>[11]</sup> hydrazone formation reactions and complex formations,<sup>[12]</sup> has some advantages.

#### **Materials and methods**

The chemicals used in the experiments were purchased commercially from Riedel, Fluka, Merck companies and used without further purification. FT-IR measurements were obtained using Perkin-Elmer Brand Spectrum 65 model FT-IR CaF<sub>2</sub> liquid cell with cell thickness (light path length) of 0.015 mm. FT-IR spectrum measurements were recorded ten scans and averaged with a resolution of  $1 \text{ cm}^{-1}$ . NMR's were obtained with Agilent Technologies brand 400 MHz NMR.



**Figure 1.** The infrared spectra of (a) chloroform in background mode, (b) benzaldehyde dissolved in chloroform in background mode (c) obtained by reading the benzaldehyde solution after recording the b spectrum as background in the range of  $1250-4000 \text{ cm}^{-1}$ . Infrared vibrations of all components in benzaldehyde solution (benzaldehyde and chloroform) were ignored by the device in spectrum (c). (Chloroform allows working in this wave numbers range due to its infrared vibrations). These three spectra explain the basis of the background defining method in the study.

#### Background defining method

Receiving an IR spectra in solutions is a slightly different than obtaining an IR spectrum of solids. Because the substance to be measured is dissolved in organic solvents, the solvent also absorbs the IR rays. Therefore, before the IR measurement the IR spectrum of the solvent has to be taken and recorded in the background mode to eliminate the vibrations come from the solvent. Then, the scanned spectrum of the solution is shown only the substance like to be measured.

The idea of background defining is, if the infrared spectra of a pure solvents can be defined as background (bg), the solutions can also be recorded as background. In Fig. 1a chloroform recorded as bg mode. In Fig. 1b is the solution of benzaldehyde in chloroform in background mode. When the spectrum is examined, the vibrations seen at 3019 and 2400 cm<sup>-1</sup> belong to chloroform, while the vibration at 2360 cm<sup>-1</sup> is caused by  $CO_2$  in the air. The vibration band at 1702 cm<sup>-1</sup> belongs to the benzaldehyde molecule. After recording the spectrum (b) as background, a new scan was performed and the spectrum (c) is obtained. Since vibrations from air and all

components (solvent, solute) in the solution are ignored by the FT-IR, the spectrum is obtained as a straight line. "Defining the background at any time in infrared measurements allows the vibration of all the components in the environment to be ignored by the device" is the basis of the bg definition method.

Organic solvents are compounds with certain organic functional groups therefore there are IR regions where they give very strong absorbance. If the sample to be measured gives absorbance at the same wavelength ranges as the solvent, it is not possible to measure these vibrations. Even if background identification is done, the IR spectrum of the solution can be measured in the wavelength range (range in which there is no severe absorbance) allowed by the solvent. In order to perform IR analysis in solution medium, the wavelength range allowed by the solvent must be determined in advance. The best working range for methyl alcohol used in this study was determined as  $1500-2000 \text{ cm}^{-1}$ .

The background defining method has been previously used to monitor some organic reactions in the liquid cell with FT-IR. The basis of this method is to ignore vibrations caused by all components in the environment at the beginning



**Figure 2.** Imine formation reaction of salicylaldehyde and aniline in ethanol. The synthesis of imine compound which is used for reduction reaction.

of the reaction by the FT-IR device. Reaction medium FT-IR measurements taken over time result only from changes in the medium. As a result, the received spectrum includes increasing and decreasing inputs in the environment.

The method, while the starting point of the reaction (mixture of input materials and solvent) is defined as background, all vibrations in the environment ignored by FT-IR. Obtaining a spectrum at any time of the reaction medium shows the vibrations of the input substances above the transmittance, while the vibrations of the product formed below the transmittance line.

In this study, the reduction reaction of the imine compound, obtained from the reaction of salicylaldehyde and aniline, with NaBH<sub>4</sub> in MeOH was investigated by FT-IR using the background defining method.

For this purpose, firstly the imine product is synthesized by the reaction of salicylaldehyde with aniline (Fig. 2), then this imine compound is converted to amine by reduction with NaBH<sub>4</sub>. This reduction reaction is also monitored by means of background defining method by FT-IR in solution.

#### Synthesis of 2-((phenylimino)methyl)phenol (pmp)

10 mmol (0.912 ml) aniline was added to the 10 mmol (1.043 ml) salicylaldehyde solution in 50 mL of ethyl alcohol. 1–2 drops of glacial acetic acid were added to the reaction mixture as a catalyst. The reaction mixture was stirred at 70 °C under reflux for 24 hours. A yellowish crude product is obtained by evaporating the solvent and recrystallized from ethanol. The structure of the product was determined by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR.



**Figure 3.** Reduction reaction of 2-((phenylamino)methyl)phenol. Reduction of the imine compound monitored by using background defining method in solution.

#### Reduction of 2-((phenylimino)methyl)phenol

The reduction reaction of the imine compound pmp (Fig. 3) was monitored in solution media by FT-IR in the liquid cell.

0.01 mol (1.97 g) of the synthesized pmp compound was taken and its solution in methanol was prepared in a 50 mL flask.

The reduction reaction was monitored in solution using the bg defining method. For this purpose, the first used solvent (MeOH) is defined as background and the range of the wavenumbers  $(2000-1500 \text{ cm}^{-1})$  is set as a default. The pmp solution prepared in methanol was taken into the liquid cell and the IR spectrum was scanned and then recorded against the methanol background. Thus, only vibrations of bmp were obtained. For further measurements the same bmp solution (reaction starting point) is recorded as bg. By this way, all vibrations originating from the pmp in solvent were reset by the device. Then, while mixing the pmp solution in a flask at ambient temperature, NaBH<sub>4</sub> was added to the medium as a certain amount of solid in order for the reduction reaction to take place. Since bg was defined at the beginning of the reaction, only changes in the reduction reaction medium were observed with FT-IR measurements.

In order to follow the reduction reaction step by step, 0.0005 mol (0.0189 g) NaBH<sub>4</sub> was added into the pmp solution, which continued to mix, and after the gas discharge process was completed, some reaction mixture was transferred to the FT-IR liquid cell and the IR spectrum of the medium was recorded. The addition of NaBH<sub>4</sub> repeatedly into the solution continued until the peak intensities in the IR spectra did not observed. The change in peak intensities is ended on the eighth addition.

![](_page_4_Figure_1.jpeg)

**Figure 4.** Infrared spectra of (a) salicylaldehyde, (b) aniline and (c) 2-((fenilimino)methyl)phenol compound. ATR-Infrared spectra of the synthesized imine compound and the input materials aniline and salicylaldehyde are given in the range of 600–4000 cm<sup>-1</sup> for comparison. The infrared spectra are represented on the % transmittance axis (arbitrary unit). The carbonyl vibration at 1661 cm<sup>-1</sup> in the infrared spectrum (a) of salicylaldehyde was converted to C = N vibration at 1614 cm<sup>-1</sup> in the spectrum (c) of the imine compound. Primary amine vibration at 3431 and 3352 cm<sup>-1</sup> in the infrared spectrum (b) of aniline was lost in the product spectrum (c).

After the reaction is completed, the solvent was evaporated and crude product 2-((phenyla-mino)methyl)phenol (pamp) was crystallized from the mixture of MeOH and EtOH  $(1/2-\nu/\nu)$ . The solution of the purified pamp compound in MeOH was prepared and IR spectrum was taken in the range of 2000–1500 cm<sup>-1</sup> and recorded for comparison with in situ IR spectrums.

#### **Results and discussion**

## Structural analysis of 2-((phenylimino)methyl) phenol (pmp)

Fig. 4a When the FT-IR spectrum of salicylaldehyde is examined, the band seen in  $2845-2750 \text{ cm}^{-1}$  originates from the symmetric and asymmetric stretching vibrations of the aldehyde hydrogen and the band seen at  $1661 \text{ cm}^{-1}$ is due to the stretching vibration of the C=O group.

Two peaks seen in the IR spectrum of aniline in Fig. 4b at 3431 and  $3352 \text{ cm}^{-1}$  results from symmetrical and asymmetrical tensile vibrations of the primary amine (-NH<sub>2</sub>). Aniline aromatic CH stress bands seen at  $3070 \text{ cm}^{-1}$  and  $3034 \text{ cm}^{-1}$ . The band in  $1618 \text{ cm}^{-1}$  is caused by the bending vibration of the  $-\text{NH}_2$  group.

In Fig. 4c, the spectrum of the imine compound pmp obtained is given. In this spectrum, it is seen that the carbonyl vibration that may be caused by salicylaldehyde and the vibrations belonging to the  $-NH_2$  group of the aniline disappear and the vibration at  $1614 \text{ cm}^{-1}$  of the imine structure of the C = N double bond occurs.

The NMR data: **1H NMR** (CDCl<sub>3</sub>,  $\delta$ , ppm) 6.95 (t, 1H), 7.05 (d, 1H), 7.29 (m, 3H), 7.41 (m, 4H), 8.63 (s, 1H, HC = N)), 13.07 (b, 1H, OH). When the <sup>1</sup>H-NMR results are interpreted, the hydrogen in the imine structure signals at 8.63 ppm, the total of nine hydrogen signals in the aromatic rings in the structure of the product and the hydrogen in the phenolic –OH group. <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm) 117.3, 119.0, 119.2, 121.2, 126.8, 129.4, 132.2, 133.1, 148.5, 161.1 (Aromatic carbon at 162.7 ppm in 13 C NMR results and 10 different C atom signals in the aromatic region supports the structure of the product and the nonlecule.

![](_page_5_Figure_1.jpeg)

**Figure 5.** Infrared spectra of (a) 2-((phenylimino)methyl)phenol (imine) and (b) 2-((phenylamino)methyl)phenol (reduced product). ATR-Infrared spectra of the synthesized imine compound and reduced product (amine) are given in the range of 600–4000 cm<sup>-1</sup> for comparison. The infrared spectra are represented on the % transmittance axis (arbitrary unit). The vibration of C = N at 1614 cm<sup>-1</sup> in the spectrum of the imine compound disappeared after reduction. Secondary amine vibration is seen at 3261 cm<sup>-1</sup> in the spectrum of the reduced product.

## Structural analysis of 2-((phenylamino)methyl) phenol (pamp)

When the IR spectrum in Fig. 5a is examined, the vibration of the C=N double bond in pmp is seen in  $1614 \text{ cm}^{-1}$ . In the spectrum of the pamp (b) N-H vibration is seen at  $1594 \text{ cm}^{-1}$ . The product has a single -N-H tensile vibration at  $3261 \text{ cm}^{-1}$  seen in Fig. 5b. These IR data show that pmp converts from imine to the amine pamp.

The NMR data of pamp: <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm) 4.42 (s, 2H), 5.30 (b, 1H, OH), 6.86 (d, 2H), 6.93 (m, 3H), 7.18 (d, 1H), 7.26 (m, 3H). The hydrogen of the -CH<sub>2</sub>- adjacent to the -NH- group appears at 4.42 ppm, and the signal in the aromatic 9 hydrogen. In addition, the fact that the hydrogen in the phenolic -OH group signals at 5.30 ppm supports the structure of the compound.

<sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) 48.7 (-CH<sub>2</sub>-), 115.9, 116.6, 120.0, 120.8, 122.9, 128.7, 129.2, 129.4, 147.2, 156.7 (Aromatic carbon atoms). <sup>13</sup>C NMR results, the aliphatic  $-CH_2$ - carbon and 10 different carbon atoms adjacent to the secondary amine group at 48.7 ppm also support the molecular structure.

## Investigation of pamp compound formation reaction with FT-IR simultaneously

In Fig. 6, spectrum (a) shows the IR spectra of methanol bg pmp (c) product (pamp). The spectrum (b) each IR spectrum illustrates a scan of the reaction media.

Focusing on Fig. 6b, it is seen that there are bands below and above the transmittance line since the starting point of the reaction is defined as background. While the vibrations above the transmittance line belong to the input substance (pmp), the bands bellow of the transmittance line are the vibrations of the product (pamp). The vibration of the C=N double bond observed in the spectrum (b) at  $1614 \text{ cm}^{-1}$  increases on the transmittance line with the addition of NaBH<sub>4</sub>. This indicates that the pmp is decreasing in the reaction medium. The increase of a vibration band at  $1604 \text{ cm}^{-1}$  below the transmittance line indicates that the amount of the pamp is

![](_page_6_Figure_1.jpeg)

**Figure 6.** The infrared spectra of (a) 2-((phenylimino)methyl)phenol, (b) reaction media, (c) pure 2-((phenylamino)methyl)phenol. Infrared spectra are given in the range of  $1500-2000 \text{ cm}^{-1}$  to allow methanol to work. Since the reaction beginning solution (methanol and imine) is defined as background, vibrations have occurred below and above the transmittance line with the addition of sodium borohydride. Vibrations below the transmittance line belong to the product (amine) and vibrations above the transmittance line belong to the input substance (imine).

increasing by the addition of NaBH<sub>4</sub>. The reason why the vibration below the transmittance line of the product does not increase as much as at  $1594 \text{ cm}^{-1}$  is that the peak at  $1589 \text{ cm}^{-1}$  overlaps by the input material decreases at the same time and we see the difference between these two vibrations.

#### Conclusions

The basis of the BG method is (blind reading) process used to ignore any interference before the IR spectrum of the media scanned. In the study, bg identification process was made for the input materials and the vibrations originating from all the substances in the environment were reset by the device and only the changes in the reaction medium were examined.

Reduction reactions of imine compounds to amine are available in the literature.<sup>[13]</sup> However, background defining method previously used in the monitoring of imine formation reactions,<sup>[14]</sup> complex formation reactions and hydrazone formation reactions<sup>[15]</sup> this study is the first time applying the method on the reduction reaction. The advantages of this in situ reaction monitoring method over other conventional reduction reactions can be listed as follows:

- Before the reduction process, the imine solution of the is defined as bg and so the vibrations of any components in the environment are eliminated by resetting the background.
- While the vibration bands originating from the imine compound (reactand) rise above the transmittance line, the vibration bands from the amine (product) appear below the transmittance line. On this way, it is easier to understand increasing and decreasing component in the reaction media.
- The products formed during the reaction can be observed in the reaction medium without purification.
- The intermediate compounds formed during the reaction can also proven by the peaks not belonging to the products during the reaction.
- Since the peak heights in the IR spectrum are proportional to the amount of substance in the sample, it is possible to obtain information about the amount of the input materials and products in the environment by compearing the peak heights.

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